

Ionomeric Films of Alginic Acid

A. E. Pavlath, C. Gossett, W. Camirand, and G. H. Robertson

ABSTRACT

Transparent, flexible films could be made by casting aqueous solutions of alginic acid, but they dissolved in water. When films were made from a solution of alginic acid and multivalent ions, they were still water soluble. However, when alginic acid films were immersed in a solution of salts with multivalent ions, they dissolved in water much more slowly, if at all. Treatment with calcium and zinc resulted in films insoluble in water and their tensile strength increased by an order of magnitude. Iron and magnesium ions had little effect on properties of the films. Copper and aluminum showed intermediate effect, but treatment with cupric ion resulted in a fast crosslinking of the surface without affecting the inside of the film. This resulted in the formation of a tube when opposing surfaces were pulled apart.

Key Words: algin, films, multivalent ions, calcium, copper

INTRODUCTION

LARGE AMOUNTS OF SYNTHETIC FILMS made from polyolefins are used in food packaging and disposal of these films creates environmental problems. Several studies have shown that the biodegradation of polyolefins is very slow (Potts et al., 1972; 1973a, b; Potts, 1978; 1984). Biodegradability can be increased by incorporating biodegradable polymers, such as starch, at 10-60% (Otey and Westhoff, 1984; Griffin, 1987; Otey and Doane, 1987; Narayan, 1989; Maddever and Chapman, 1989). Most biopolymers are biodegradable, but are not easily molded. The addition of a plasticizer, such as water, can improve their moldability (Jane et al. 1993a). However, such plasticized and molded films have less desirable physico-chemical properties than synthetic polymers. Water soluble biopolymers, mostly carbohydrates, usually form films, but readily solubilize in water during usage. Permanent crosslinking of protein polymers through covalent bondings improves physico-chemical properties, but it may lessen the biodegradability (Jane et al. 1993b).

Low molecular weight, acidic, water-soluble biodegradable polymers may be crosslinked by reacting them with multivalent ions. Such crosslinking can be reversible depending on the pH of the medium and other factors. Therefore, reversible crosslinks could minimize any negative impact on biodegradability. Alginic acid, a low molecular weight copolymer of glucuronic and mannuronic acids obtained from harvested brown seaweeds, is a potential source for such application. This

polymer is nontoxic and, therefore, could be used in food packaging. It is biodegradable and soluble in water. Alginic acid can form solid, cohesive and continuous complexes with multivalent ions.

There are several possible ways to cause the interaction of acidic biopolymers with these ions. The components may be mixed and cast as a film as has been long known. In many cases gel formation is instantaneous and prevents casting, so the mixing must be carried out either in low concentration or at an elevated temperature. While the interaction of biopolymers with calcium ion has been long known, interaction with other multivalent ions is not well known. A technique using slow release of calcium to form a uniform gel has been reported (Draget et al., 1991). An alternate method of increasing the strength of gels is by immersing them into aqueous solutions of multivalent cations (Kaletunc et al., 1990). This could be adapted to a previously cast and dried alginic acid film. The concentration of the solution and the time of exposure of the film to the solution could be used to control or influence the film properties. Our objective was to develop pliable biodegradable films based on alginic acid with comparable physico-chemical properties, e.g., strength and insolubility in water, to those of synthetic polymers which are non-biodegradable.

MATERIALS & METHODS

Materials

Sodium alginate was obtained from Manugel DMB, KELCO Inc. (San Diego, CA Lot no. 520043). The available free carboxylic groups were characterized by the manufacturer as 4.82g of $\text{Ca}^{++}/100\text{g}$ alginate. The source of multivalent ions was analytical reagent quality: $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$,

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

Analytical measurements

After treatment with multivalent ions the films were air dried, selected visually for integrity and uniformity, and cut into 1.3×10.1 cm ribbons. Fragile films were discarded. Tensile strength of the films was measured in quintuplet by Instron Model 4502 Series H3033 at a relative humidity of 50% and temperature of 25°C according to ASTM D1004-94a.

The colored interaction of the alginate film with copper ion was measured with a Mark Minolta colorimeter by the intensity of the color using the Hunter L, a^* and b^* values at five locations. Extremes of these values are: for L black (−) to white (+), a^* green (−) to red (+) and b^* blue (−) to yellow (+).

The aqueous solubility of the films was determined by a qualitative method. Films ($1.3 \times 3.0 \text{ cm}^2$) were placed in 10 mL of distilled water, an excess amount relative to the original solution, and visually observed at regular time intervals for appearance of dissolution.

Film preparation

Sodium alginate film. Sodium alginate (4.5g) was mixed with 50 mL of ethanol at room temperature ($\sim 20^\circ\text{C}$) to facilitate full dissolution, and then 550 mL of water was added to provide a 0.75% solution. The resulting viscous solution was deaerated under vacuum and then poured into four $10.1 \times 15.2 \text{ cm}^2$ frames. The water and ethanol was evaporated at room temperature aided by cross-flowing air at $\sim 2 \text{ m}^3/\text{min}$. The drying time was 14h. When drying was carried out at 55°C in a drying chamber designed for the preparation of electrophoresis gels, drying time was reduced to 2.5h.

Since the films were quite fragile, glycerin was added to the solution. The amount, based on previous studies (Owens and Schultz, 1952), was 40% of the dry weight of the alginate and resulted in pliable films. The thickness of the dry films was 0.25-0.30 mm.

Films by immersion. The dry films ($10.1 \times 15.2 \text{ cm}^2$) were then dipped in 200 mL of aqueous solutions of the various reagents. Three concentrations, 2, 5 and 10%, and four dipping times, 5, 15, 30 and 60 min were applied. The amount of multivalent ions at 2% concentration represented about $10 \times$ the stoichiometric amount. The films then were

The authors are affiliated with the U.S. Dept. of Agriculture, Agricultural Research Service, Western Regional Research Center, 800 Buchanan St., Albany, CA 94710.

air dried at room temperature.

Films by mixing. Sodium alginate (3.75g) was mixed with 50 mL of ethanol, and then with 300 mL of water containing 1.5g glycerin at 50°C. Then 550 mL aliquots of solutions containing 25, 50, 75 or 100% of the stoichiometric amount of ions, which were also pre-warmed to 50°C, were added gradually. The resulting viscous solutions were deaerated under mild vacuum and then poured into drying frames. Drying continued for 12-16h because of the large amount of solvent to be evaporated from these dilute solutions and the rapidly increasing viscosity of the solutions.

RESULTS & DISCUSSION

THE AIR-DRIED FILMS FROM SODIUM ALGinate were transparent and pliable. However, they were not moisture resistant and readily dissolved in distilled water within minutes. When the films had been immersed in multivalent ion solutions, the crosslinking of the carboxyl groups considerably lessened the solubility of the films. However, the crosslinking was not instantaneous throughout the film. It was a function of time and concentration. Result of immersing the films in solutions of salts for varying times were compared (Table 1). We assumed that when the films were immersed in these solutions two competitive processes occurred. The dissolution of the sodium alginate was very rapid and the diffusion of the multivalent ion which crosslinked the surface and reduced the rate of dissolution was slower. If the concentration of the multivalent ion was low, the first process, i.e., dissolution would be dominant. Conversely, increasing ion concentration would counteract the dissolution. A 2% concentration was not sufficient to desolubilize the films, except for copper ions. Higher ion concentrations resulted in considerable less solubility, in most cases giving films that did not dissolve in distilled water even after 3 weeks. The treatment with magnesium salt did not result in acceptable films at any concentration or treatment time. With zinc and iron, higher concentrations (10%) were needed to cause insolubility of the film.

The changes in film color (b values, Fig. 1 and 2) indicated the incorporation of copper in the film and suggest substantive saturation at about 8%. Unexpectedly, films crosslinked by immersing in copper solutions for <30 min and at <5% Cu-salt (by wt), formed tubes when the films were gently pulled apart or pinched from opposite sides. This suggests that the film surface was highly crosslinked and strengthened, but the inside of the film was so highly hydrated that it lost its cohesiveness. This was noted only with copper ions.

The properties of films obtained when alginic acid solution was mixed with multivalent ions depended greatly on the concentrations, and temperatures of mixing. Without addition of glycerin, these films were unac-

Table 1—Insoluble film formation from Na-alginate films immersed in multivalent ion solutions^a

Ion	Conc %	5 min		15 min		30 min		60 min	
		w/g	wo/g	w/g	wo/g	w/g	wo/g	w/g	wo/g
Al	2						+		
	5	+	+	+	+	+	+		
	10	+		+		+		+	
Ca	2								
	5		+	+	+	+	+		
	10	+	+	+	+	+	+	+	
Cu	2		+		+		+		+
	5			+	+	+	+		+
	10					+	+	+	
Fe	2								
	5				+				
	10		+	+	+	+	+	+	
Zn	2								
	5				+				
	10	+	+	+	+	+	+	+	+

^aw/g= glycerin added, wo/g no glycerin added.

+ homogenous, continuous and visually insoluble film.

ceptably fragile under all conditions. When mixing was done at room temperature (~20°C), immediate gel formation occurred and no films could be cast. An increase to 50°C was needed so that the viscous solution could be poured into the frames for casting. Resulting films (Table 2) were very fragile when components were used in stoichiometric ratio. All films, with exception of those formed from zinc, were visually opaque. The transparency increased somewhat at 75% stoichiometric ratio, but the films were still unacceptable. At 50% ratio only calcium, copper and zinc gave pliable films with some opacity. Only the 25% ratio resulted in completely transparent films with all ions but aluminum. However, in each case the films readily dissolved in water within 30 min in contrast to the stable films created from water-soluble films after dipping them in multivalent ionic solutions. We hypothesize that elevated temperature needed for keeping the mixture fluid,

altered the structure of the alginic acid. This could have been by lowering the molecular weight and/or reorienting the configuration, as suggested by the lowered viscosity after heating the solutions to 50°C. Since the solubility of these films made them unacceptable for the purpose of this investigation, no further attempt was made to confirm this. Interestingly, when these soluble films (0.25 stoichiometric ratio) obtained by mixing of the components were immersed into calcium solution they became insoluble in water.

The tensile strength and elasticity of the films obtained by various methods were compared (Table 3). Treatment with calcium, at 5% and 10% concentrations, yielded the greatest increases in strength of alginic acid films. After immersing in calcium and copper, the films shrank irregularly to 50-60% of the original, while other ions resulted in smoother films after immersing. The effect of time also varied with the type of ions and whether glyc-

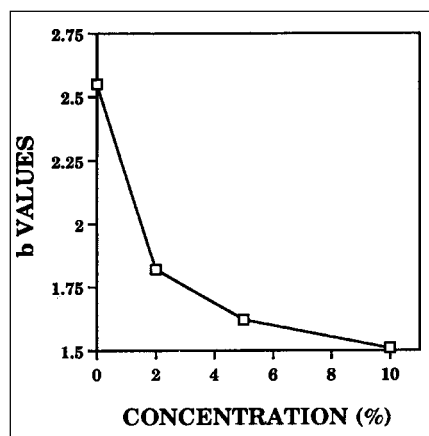


Fig. 1—Intensity of blue color as related to concentration of cupric chloride after 30 min immersion. Note: lower b=increasing blue intensity.

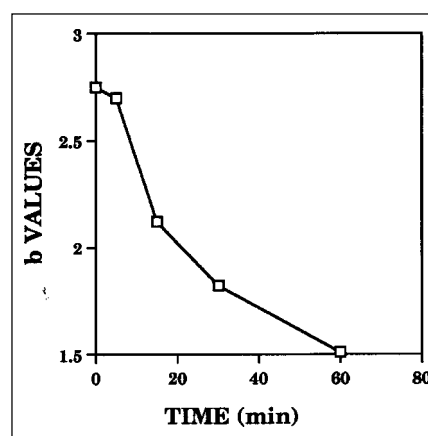


Fig. 2—Intensity of blue color as related to time of immersion in 2% cupric chloride solution. Note: lower b=increasing blue intensity.

Table 2—Visual appearance of films formed from Na-alginate and multivalent ion salts solutions

Stoichiometric ratio	Ca ⁺⁺	Zn ⁺⁺	Cu ⁺⁺	Fe ⁺⁺	Al ⁺⁺⁺
1.0	opaque fragile	some opacity wrinkled	opaque fragile	opaque fragile	opaque fragile
0.75	opaque fragile	some opacity wrinkled	some opacity	opaque wrinkled	opaque fragile
0.5	some opacity smooth	almost clear smooth	almost clear fragile	opaque fragile	opaque
0.25	clear smooth	clear smooth	clear smooth	clear flat	opaque fragile

Table 3—Mechanical properties of films formed from Na-alginate films by multivalent ion treatments at maximum load as measured by Instron

Concentration of ions						
Ion	Time min	Glycerin	5%		10%	
			Stress ^a Mpa	Strain %	Stress Mpa	Strain %
Al	5	No	30.92	1.52		
		Yes	19.61	1.35	48.57	2.22
	15	No	37.00	1.23		
		Yes	31.00	0.96	51.67	1.40
	30	No	24.13	0.72		
		Yes	40.27	1.06	24.93	0.89
Ca	60	Yes			23.42	1.21
		No	71.62	3.04	96.96	3.02
	5	Yes	41.11	3.47	48.85	4.49
		No	87.32	3.52	103.20	2.83
	15	Yes	62.43	3.56	55.94	2.18
		No	65.92	3.66	88.50	2.78
Cu	30	Yes	47.95	4.14	52.88	3.73
		No			132.40	2.59
	60	Yes			73.28	2.84
		No	48.76	4.05		
	15	Yes	33.74	2.82		
		No	96.38	4.42	19.44	2.24
Zn	30	Yes	19.44	2.24	53.96	3.41
		No			18.65	2.16
	60	Yes			89.78	3.28
		No			62.69	2.35
	5	Yes			34.43	2.19
		No			79.42	2.65
	15	Yes			34.8	2.51
		No			71.72	4.19
	30	Yes			39.03	2.83
		No			64.39	1.98
	60	Yes			49.55	3.69
		No				

^aStress denotes maximum load where test sample broke. Strain indicates percent elongation at maximum load. For untreated dry sodium alginate film these were 5.6 Mpa & 1.62% without glycerin and 6.1 Mpa and 11.8% without glycerin. Cellulose acetate and polyethylene films were 35.58 Mpa and 3.11% and 21.28 Mpa and 153.5% respectively.

erin was used. No absolute conclusion was apparent, but a qualitative trend observed. The tensile strength quickly reached a maximum after 5-15 min of treatment with calcium at 5%. At 10%, the maximum was reached at shorter times and longer exposure frequently decreased the value. The addition of glycerin as a plasticizer may decrease the tensile

strength, but the percentage of elongation at breakage did not necessarily increase in the same proportion, and in some cases even decreased.

CONCLUSION

ALGINIC ACID SOLUTION MAY BE CAST TO form transparent films, but they had low

strength and redissolved in water. When the casting solution was mixed with various multivalent ions in less than stoichiometric ratio soluble films were also formed. However, when dry films cast from alginic acid were immersed in a solution of multivalent ions, the resulting films were resistant to dissolution in water, and depending on the applied ion, had higher tensile strength. This was especially notable with calcium. The strength and insolubility of dry films cast from multivalent ion/alginate solutions were also improved by ion solution immersion. Unusual films from Cu⁺⁺ suggested that study of the exposure method may result in films with unique properties.

REFERENCES

- Drager, K.L., Ostgaard, K., and Smidsrod, O. 1991. Homogenous alginate gels: A technical approach. *Carbohydrate Polymers* 14: 159-178.
- Griffin, G.J.L. 1987. Degradable plastic films. In *Proceedings of Symposium on degradable plastics*, p. 47-49. The Society of Plastics Industry, Inc., Washington, DC.
- Jane, J.L., Lim, S.T., and Paetau, I. 1993a. Degradable plastics made from starch and protein. In *Biodegradable Polymers and Packaging*, C. Ching, D.L. Kaplan and E.L. Thomas (Ed.), p. 63-73. Technomic, Lancaster.
- Kaletunc, G., Nussinovitch, A., and Peleg, M. 1990. Alginate texturization of highly acid fruit pulps and juices. *J. Food Sci.* 55: 1759-1761.
- Maddever, W.J. and Chapman, G.M. 1989. Modified starch based biodegradable plastics. *Plastics Engr.* July: 31-34.
- Narayan, R. 1989. Starch based plastics, in *Assessment of Biobased Materials*, H.L. Chum (Ed.), p. 7.1-7.25. Report SERI/TR-234-3610, Solar Energy Research Institute, Colorado.
- Otey, F.H. and Doane, W.M. 1987. Starch-based degradable plastic films. In *Proceedings of Symposium on Degradable Plastics*, p. 39-40. The Society of Plastics Industry, Inc., Washington, DC.
- Otey, F.H. and Westhoff, R. 1984. Starch-based films. I&EC Products Research Development, p. 284-287. American Chemical Society, Washington, DC.
- Owens, H.S. and Schultz, T.H. 1952. Method of coating foods with pectinate and pectate films U.S. patent 2,611,708.
- Potts, J.E. 1978. Biodegradation. In *Aspects of Degradation and Stabilization of Polymers*, H.H.G. Jellinek (Ed.), p. 617-658. Elsevier, New York.
- Potts, J.E. 1984. Plastics, environmentally degradable. In *Kirk-Othmer Encyclopedia of Chemical Technology*, Suppl. Vol., M. Rayson (Ed.), p. 626-668. Wiley Interscience, New York.
- Potts, J.E., Clendinning, R.A., Ackart, W.B., and Niegisch, W.D. 1972. The biodegradability of synthetic polymers. Technical Paper, Regional Technical Conference, Society Plastics Engineers, Chicago Section, p. 63-70.
- Potts, J.E., Clendinning, R.A., and Ackart, W.B. 1978a. The effect of chemical structure on the biodegradability of plastics. In *Degradation of Polymers and Plastics*, p.12.1-12.10. Institute of Electrical Engineers, London.
- Potts, J.E., Clendinning, R.A., Ackart, W.B. and Niegisch, W.D. 1978b. The biodegradability of synthetic polymers. In *Polymers and Ecological Problems*, J. Guillet (Ed.), p. 61-80. Polymer Science & Technology, Vol 3, Plenum Press, New York.
- Ms received 2/6/98; revised 6/28/98; accepted 8/17/98.